

A SPECTROSCOPIC STUDY OF THE HYDROLYSIS PRODUCTS OF ARYLTELLURIUM TRIHALIDES

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SUMMARY

The hydrolysis of aryltellurium trihalides to aryltellurium oxide halides in neutral aqueous media is considered to proceed in a stepwise manner in which the first stage involves the formation of a monomeric species. In alkaline media the initially isolated hydrolysis product analyses as (*p*-EtOC₆H₄)TeO(OH) and on treatment with dilute acid, affords the known (*p*-EtOC₆H₄TeO)₂O.

The infrared spectra are assigned in the low frequency region for the compounds RTe(O)X (X = halogen), RTeO(OH) and (RTeO)₂O. It is argued that the probable coordination number for tellurium in RTe(O)X is four, and that a ring structure is likely. The preparation of the salts (C₅H₅NH⁺)(RTeCl₄⁻) is reported and the anions are considered to have square-based pyramidal structures of approximately C_{4v} symmetry. The reaction of (C₅H₅NH⁺)(PhTeCl₄⁻) with acetone affords Ph(CH₃-COCH₂)TeCl₂.

INTRODUCTION

The hydrolysis of aryltellurium trihalides has been the subject of some previous investigations¹⁻³. There is general agreement that hydrolysis in neutral aqueous media affords a product of stoichiometry RTe(O)X (X = Cl, Br; R = aryl) whereas the hydrolysis of RTeI₃ by hot water leads to less well defined products in most cases³. The use of an alkaline medium has variously been said to lead to RTe(OH)₃¹ (R = *p*-MeOC₆H₄⁻), RTe(O)OH² and (RTeO)₂O³. In all cases¹⁻³ the products of the alkaline hydrolysis were treated with dilute acid prior to analysis. It is now generally accepted that the anhydride formulation is correct³. No attempt has been made to discuss the structure of these hydrolysis products and, apart from one speculative scheme⁴, no discussion of the mechanism of hydrolysis has been given.

In this paper we attempt to extend our previous spectroscopic investigations⁵ to the hydrolysis products. We also attempt to gain more insight into the probable course of the reaction.

EXPERIMENTAL

General

Infrared spectra were recorded for Nujol mulls with Perkin-Elmer 457 (4000-

250 cm^{-1}) and 225 (400–200 cm^{-1}) spectrometers. Far infrared spectra were recorded in triplicate using an R.I.I.C. FS 720–FS 200 interferometer. The samples were Nujol mulls in polythene cells and the spectra were computed to a resolution of 2 cm^{-1} with the University ICL 1905 computer. The interferometer was calibrated with water vapour. Raman spectra were recorded for solid samples with He/Ne laser excitation using a Coderg PH 1 instrument*. Analysis for tellurium was by a recently developed method⁶ using a Perkin–Elmer model 303 Atomic Absorption spectrophotometer.

The methods we have used to hydrolyse the aryltellurium trihalides are based on those employed by Petraghani and Vicentini³. We restricted our attention to the cases where the aryl group was phenyl- or *p*-ethoxyphenyl- (*p*-EtOC₆H₄-). We note that Reichel and Kirschbaum² report products, *e.g.* (*p*-EtOC₆H₄)Te(O)Cl which decompose between 400 and 500°C whereas Petraghani and Vicentini report definite melting points (224–226°). Our experience has been that unless scrupulous attention is paid to the purification of the starting material, (*p*-EtOC₆H₄)TeCl₃, hydrolysis products of indefinite melting points are obtained.

We have checked for completion of the hydrolysis reaction by precipitating the released halide as the silver salt. In view of the fact that previous reports have not been in complete agreement we give brief details of the experimental methods we have used to synthesise the various compounds whose spectra are discussed.

Phenyltellurium oxide chloride

Phenyltellurium trichloride (0.84 g) was magnetically stirred with cold water (20 ml) for 45 min. The white powder-like product (0.57 g) was filtered and dried *in vacuo* over P₄O₁₀. (Found: C, 28.9, H, 1.99. C₆H₅ClOTe calcd.: C, 28.1; H, 1.95%). M.p. 226–228° (shrank), 280° (lit.³, 250°). Analysis of the filtrate for chloride indicated the release of two moles of chloride per mole of PhTeCl₃.

Phenyltellurium oxide bromide

Phenyltellurium tribromide (0.53 g) was stirred with cold water (25 ml) for 2.5 h. The pale yellow product (0.29 g) was filtered and dried *in vacuo* over P₄O₁₀. (Found: C, 26.8; H, 2.20. C₆H₅BrOTe calcd.: C, 24.1; H, 1.8%). M.p. 218–222° (lit.³, 247–249°). Analysis of the filtrate for bromide ion confirmed the release of two moles of bromide per mole of PhTeBr₃.

Attempted preparation of phenyltellurium oxide iodide

When phenyltellurium triiodide⁵ was stirred with cold water, only slight reaction had occurred after 46 h. The use of hot water gave a mixture of products including some tellurium metal.

(p-Ethoxyphenyl)tellurium oxide chloride

Pure (*p*-EtOC₆H₄)TeCl₃⁷ (1.0 g) was stirred with cold water (40 ml) for 30 min. The white product was filtered and dried *in vacuo* over P₄O₁₀. (Found: C, 32.5; H, 2.83. C₈H₉ClO₂Te calcd.: C, 32.0; H, 3.00%). M.p. 222–225° (lit.³, 224–226°). Analysis of the filtrate confirmed the release of two moles of chloride per mole of (*p*-EtOC₆H₄)TeCl₃.

* We thank Dr. D. M. Adams, University of Leicester, for access to this instrument.

(p-Ethoxyphenyl)tellurium oxide bromide

(*p*-Ethoxyphenyl)tellurium tribromide (0.59 g) was stirred with cold water (50 ml) for 45 min with no visible change in colour. The mixture was warmed to 50° causing a rapid change in colour to pale yellow of the solid material. The warming was continued for 30 min after which the product (0.35 g) was filtered and dried *in vacuo* over P₄O₁₀. (Found: C, 29.8; H, 3.34. C₈H₉BrO₂Te calcd.: C, 27.9; H, 2.6%). M.p. 210–215° (lit.³ 233–236°). Analysis of the filtrate for bromide confirmed the stoichiometry of the reaction. We also found that the same product was obtained if the tribromide was stirred overnight with cold water.

(p-Ethoxyphenyl)tellurium oxide iodide

(*p*-Ethoxyphenyl)tellurium triiodide⁸ (1.7 g) was heated under reflux with water (50 ml) for 4 h. The black crystals changed to red-brown and the product (1.0 g) was filtered and dried *in vacuo* over P₄O₁₀. (Found: C, 24.8; H, 2.27, C₈H₉IO₂Te calcd.: C, 24.5; H, 2.32%). M.p. 170°. The same product may be obtained by stirring the triiodide with cold water for a minimum of 48 h.

Attempts to isolate intermediate products

The reaction times were varied over wide ranges for the above experiments. For short reaction times erratic analytical data were obtained and infrared analysis of the products suggested mixtures rather than new compounds. In one experiment with (*p*-EtOC₆H₄)TeI₃ it was found that only one mole of iodide was released, however spectroscopic analysis showed the tellurium-containing product to be a mixture of (*p*-EtOC₆H₄)TeI₃ and (*p*-EtOC₆H₄)Te(O)I rather than the hoped for [(*p*-EtOC₆H₄)TeI₂]₂O. The replacement of water by aqueous ethanol in the above experiments gave the same pattern of results.

Hydrolysis in alkaline media

Our experiments were restricted to the (*p*-ethoxyphenyl)tellurium trihalides which were treated with 10% sodium carbonate solution. A typical experiment involved stirring pure (*p*-EtOC₆H₄)TeCl₃ (1.2 g) with 10% sodium carbonate solution (40 ml) at room temperature for 2 h. The reaction mixture was divided into two parts: (a) the white product was filtered and dried *in vacuo* over P₄O₁₀; (b) the mixture was acidified with dilute acetic acid and the stirring was continued for 1 h after which the second product was filtered and dried over P₄O₁₀. Separate experiments involving analysis of the filtrates for chloride established that in both cases all the chloride was released from the starting trihalide. Use of shorter reaction times afforded products whose analytical and spectroscopic data were difficult to reproduce. (Found: product (a); C, 33.9; H, 3.50. M.p. 199–201° (shrank), 235–240° (dec.): Product (b); C, 34.7; H, 3.47. M.p. 234–238° (dec.) Product (a), which shows ν(OH) at 3060 cm⁻¹ (hydrogen bonded) has an analysis corresponding closely to that expected for (*p*-EtOC₆H₄)TeO(OH). C₈H₁₀O₃Te calcd.: C, 34.1; H, 3.6%. Product (b) corresponds to the "anhydride" [(*p*-EtOC₆H₄)TeO]₂O. C₁₆H₁₈O₅Te₂ calcd.: C, 35.1; H, 3.3%.)

Reaction of aryltellurium trichlorides with pyridine in benzene

Phenyltellurium trichloride (0.5 g) was added to dry benzene (80 ml) containing freshly distilled pyridine (2 ml) and set aside for 48 h. The white product (0.6 g) was filtered and dried. The product was treated with acetone to afford an insoluble residue

of phenyltellurium oxide chloride. The acetone solution was concentrated and then treated with petroleum ether (40–60°) to give white crystals (0.15 g) (a). Further treatment of the filtrate with petroleum ether afforded a second crop of white crystals (b). Solid (a) proved to be pyridinium phenyltetrachlorotellurate(IV), (PyH⁺)(PhTeCl₄⁻). (Found: C, 31.5; H, 3.12; N, 3.14. $\nu(\text{NH})$ 3220, 3165 cm⁻¹, $\Lambda_m(10^{-3} M \text{ in MeNO}_2)$ 90 $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$, m.p. 245–247° (dec.) C₁₁H₁₁Cl₄NTe calcd.: C, 31.0; H, 2.60; N, 3.3 %.) Solid (b) contained no nitrogen and was a non-electrolyte in nitromethane (Λ_m 7 $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) and was identified as a reaction product of PhTeCl₄⁻ and acetone, i.e., Ph(CH₃COCH₂)TeCl₂. (Found: C, 32.1; H, 3.34; N, 0.00. $\nu(\text{CO})$ 1705 cm⁻¹ vs(sharp). M.p. 113–114°. C₉H₁₀Cl₂OTe calcd.: C, 32.5; H, 3.01 %.)

A similar reaction sequence with (*p*-EtOC₆H₄)TeCl₃ afforded (PyH⁺)[(*p*-EtOC₆H₄)TeCl₄⁻]. (Found: C, 33.3; H, 3.27; N, 3.0; Te, 26.7. $\Lambda_m(10^{-3} M \text{ in MeNO}_2)$ 77 $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$. M.p. 212–214° dec. C₁₃H₁₅Cl₄NO₂Te calcd.: C, 33.2; H, 3.20; N, 3.0; Te, 27.1 %.)

RESULTS

Spectroscopic data for the compounds we consider are given in Tables 1 (phenyl compounds) and 2 (*p*-ethoxyphenyl compounds).

We found that in general our preparative results, all of which were reproducible, parallel those of Petragnani and Vicentini³, however we do differ from those authors in some points of detail. Thus we occasionally observe different behaviour on heating the compounds and, whereas we agree that it does not appear possible to prepare PhTe(O)I pure, we did succeed in synthesising (*p*-EtOC₆H₄)Te(O)I which, apart from (*p*-MeOC₆H₄)Te(O)I³, is the only oxyiodide to be prepared to date. We have confirmed that a product [(*p*-EtOC₆H₄)TeO]₂O is obtained from the alkaline hydrolysis of (*p*-EtOC₆H₄)TeCl₃ after treatment with acetic acid. However another product may also be reproducibly prepared which, according to infrared data, contains OH bonds and the analysis of which corresponds to (*p*-EtOC₆H₄)TeO(OH). The compound is converted to the anhydride on treatment with dilute acetic acid.

We failed to isolate any product of the hydrolysis corresponding to a stage intermediate between RTeX₃ and RTe(O)X thus the intervening stages appear to be fast, the limited solubility of RTeX₃ in water is probably the rate determining factor. In an attempt to use a Lewis base other than water to break the bridging halogen bonds in RTeX₃, we reacted pyridine with phenyl- and (*p*-ethoxyphenyl)tellurium trichlorides. Although our reagents were supposedly "dry" they contained sufficient water to hydrolyse some RTeX₃ to RTe(O)X. The hydrogen chloride released reacted with RTeX₃ to afford RTeCl₄⁻ which was subsequently isolated as a pyridinium salt having a molar conductivity in nitromethane solution characteristic of a 1/1 electrolyte. Recrystallisation of (PyH)(PhTeCl₄) from an acetone-containing medium led to the isolation of the new compound Ph(CH₃COCH₂)TeCl₂. The condensation of mono-organotellurium trihalides with methyl ketones is well known yet surprisingly this example of the reaction has not been previously reported. Interestingly enough the *p*-ethoxyphenyl salt did not give the corresponding compound when treated under the same conditions. We made attempts to prepare the analogous sulphur compounds, RTe(S)X, by treating alcohol solutions of RTeX₃ with dry H₂S but immediate reduction to ditelluride was observed.

TABLE I
THE LOW-FREQUENCY VIBRATIONAL SPECTRA OF PHENYLTELLURIUM COMPOUNDS

PhTe(O)Cl^a	PhTe(O)Br^a	$\text{PhTe(CH}_2\text{COCH}_3\text{)Cl}_2$	$(\text{PyH}^+)(\text{PhTeCl}_4)^b$ IR	$(\text{PyH}^+)(\text{PhTeCl}_4)^b$ Raman	Assignment
715 s	704 s				} Tellurium-oxygen modes
605 s	592 s				
498 s	495 s				
424 s	411 s				
312 m-s	304 s				
259 m-s	251 s	260 s ^c	264 s	256 (sh)	Phenyl t or v(TePh)
234 m-s	234 m	Masked	Masked		Phenyl u
207 m	208 m	214 s	182 (sh)		Phenyl x
196 m	165 s	160 m			Phenyl x'
277 s	185 s	260 s ^c 250 s ^c	284 m 227 vs 152 m	249 m-s 280 s 220 (br, sh)	v(Te-halogen)
150 m	136 m	530 m 131 m 117 w			δ (Te-halogen) v(Te-alkyl) Other bands

^a PhTe(O)Cl and PhTe(O)Br gave unsatisfactory Raman spectra, ^b PyH^+ pyridinium cation, ^c Overlap of bands.

TABLE 2

LOW FREQUENCY VIBRATIONAL SPECTRA OF SOME (*p*-ETHOXYPHENYL)TELLURIUM COMPOUNDS (R₂Te COMPOUNDS)

R ₂ Te(O)Cl IR	R ₂ Te(O)Cl Raman	R ₂ Te(O)Br IR	R ₂ Te(O)I ^a IR	R ₂ TeCl ₃ + 10% Na ₂ CO ₃ ^b	R ₂ TeCl ₃ + 10% Na ₂ CO ₃ ^c	Assignment
719 s		704 s	688 m	715 s	705 s	Te-O modes
602 s	603 m	590 s	575 s	695 (sh)	680 s	
500 s ^d		505 (sh)	482 s	568 s	555 s	
425 s	425 s	415 s	400 m	380 m-s	393 m-s	
308 s	313 w	303 s	298 w-m			
248 s	249 vs	187 vs	115 w(?)			
145 w	145 w					
323 s	323 w	321 s	318 m	302 s	312 m-s	
272 s	271 w	264 m	264 w-m	236 s	264 s(br)	
217 m		218 s	218 m	218 s	227 s	
205 m			180 s		192 s	Bands arising from R = <i>p</i> -EtOC ₆ H ₄
168 m	168 s ^e	153 m	172 (sh)	174 s	172 (sh)	
139 w			137 m	148 w		
119 m	121 m	100 w-m		112 m	118 m-s	
87 m		57 w-m				

^a (*p*-EtOC₆H₄)Te(O)I absorbed at the laser frequency and it was not possible to obtain a Raman spectrum.

^b Without acidification with acetic acid. ^c After acidification with acetic acid. ^d Mixed with R mode. ^e Overlap with laser line.

broad band centred on 3060 cm⁻¹ which we assign as ν(OH). The low frequency and the breadth of the band suggest hydrogen bonding to play an important part in this structure. The spectra of the two pyridium salts are very similar and are dominated by two strong vibrations above 200 cm⁻¹ which may be assigned as ν(TeCl). The bands occur at lower frequency than those of the terminal Te-Cl bonds of the parent trichlorides. However this is to be expected for an anionic complex compared with a neutral species. The spectrum of Ph(CH₃COCH₂)TeCl₂ is unremarkable and is consistent with the established distorted four-coordinate structure of other diorgano-tellurium dihalides¹¹. The assignment of ν(Te-alkyl) at 530 cm⁻¹ may be compared with that of ν(TeC) at 534 cm⁻¹ for Me₃TeBr¹².

Structural considerations

Vibrational spectroscopic data alone cannot offer definitive answers to the structural problems posed, however it is possible to make some progress towards a solution of the problem.

(a). *Aryltellurium oxide halides*. A structural model must be able to account for the rich spectrum associated with tellurium-oxygen modes and for the slight solubility of the material. In addition the position of the tellurium-halogen modes are of interest since they are considerably lower in frequency than those observed for PhTeX₃ and (*p*-EtOC₆H₄)TeX₃⁵. This may be due to one of three factors—an increased coordination number for tellurium in RTe(O)X₃, the involvement of the halogen atom in bridge bonds, or the formation of weaker (longer) tellurium-halogen

bonds in $\text{RTe}(\text{O})\text{X}$. We believe the coordination number of tellurium in RTeX_3 to be five⁵, thus to evaluate the first possibility we must invoke a coordination number for tellurium of at least six in $\text{RTe}(\text{O})\text{X}$. We find it difficult to visualise plausible structures involving six-coordinate tellurium and furthermore this coordination environment would violate the hypothesis of Wynne and Pearson¹³ which argues against the formation of bonds *trans* to the organic group. We have found this a workable hypothesis in the past⁵ and are therefore led to consider other structural possibilities. The tellurium halogen modes appear to be too simple and too high in frequency to convincingly imply bridging halogen atoms, however the frequencies we assign as $\nu(\text{TeX})$ are very close indeed to those reported for a wide range of diaryltellurium dihalides¹¹. Thus the tellurium atom may well in fact exist in a distorted four-coordinate environment such as that illustrated in Fig. 1 in which the axial bonds in the ψ -trigonal bipyramidal

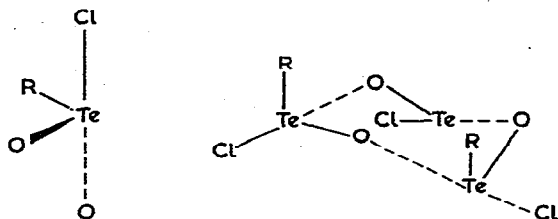


Fig. 1. Suggested environment of tellurium in $\text{RTe}(\text{O})\text{X}$.

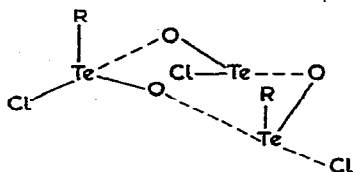


Fig. 2. Illustration of a possible ring structure for $\text{RTe}(\text{O})\text{X}$.

arrangement are longer than the equatorial bonds. We believe that a ring structure is most probable since this would account for the complexity of the tellurium–oxygen vibrations and such a structure may also account for the slight solubility rather better than a highly polymeric model. Thus we conclude that the model which most reason-

TABLE 3

THE LOW-FREQUENCY VIBRATIONAL SPECTRA OF ORGANOTETRACHLOROTELLURATES(IV)

$(\text{C}_5\text{H}_5\text{NH})(\text{PhTeCl}_4)$		$(\text{C}_5\text{H}_5\text{NH})[(p\text{-EtOC}_6\text{H}_4)\text{TeCl}_4]$		$(\text{Ph}_4\text{As})(\text{PhTeCl}_4)^a$		Ph_4AsBr	Assign- ment
IR	Raman	IR	Raman	IR	Raman	IR	
284 m	280 s 249 m-s	284 s	284 s 254 s	280 s(sh)	284 vs 248 s		A_1^+ B_1^+ E^+
227 vs	220 (br, sh)	231 vs	228 (br, sh)	227 (sh) 396 w 363 s 347 s	220 (br, sh)	398 w 363 s 348 s 342 s	Ph_4As^+
264 s 182 (sh) 152 m	256 (sh)	262 s 211 s 147 m	262 (sh)	260 s 250 m 235 m-s			"R" modes

^a The salt $(\text{Ph}_4\text{As})(\text{PhTeCl}_4)$ was prepared by the direct reaction of tetraphenylarsonium chloride and phenyltellurium trichloride in abs. ethanol. (Found: C, 49.6; H, 3.6. $\text{C}_{30}\text{H}_{25}\text{AsCl}_4\text{Te}$ calcd.: C, 49.5; H, 3.4%.)

ably accounts for the available data is one which involves four-coordinate tellurium atoms in a ring structure. The feasibility of this model is illustrated in Fig. 2. We do not believe that the complex spectra of (*p*-EtOC₆H₄)TeO(OH) and of [(*p*-EtOC₆H₄)-TeO]₂O justify further discussion at this stage.

(b). C₅H₅NH⁺RTeCl₄⁻ (R=Ph or *p*-EtOC₆H₄⁻). The anions of these salts are analogous to the well known MeTeI₄⁻ which occurs in the β form of Me₂TeI₂ [(Me₃Te⁺)(MeTeI₄⁻)]¹⁴ and consequently a square pyramidal structure is most probable. Assuming free rotation about the tellurium-carbon bond the symmetry of the anion approximates to C_{4v} for which two infrared-active tellurium-chlorine stretching vibrations are anticipated (A₁+E) together with three Raman bands (A₁+B₁+E). In Table 3 we isolate the infrared and Raman spectra of the pyridinium salts but offer more complete assignments for (C₅H₅NH)(PhTeCl₄) in Table 1. We have also prepared the salts (Ph₄As⁺)(PhTeCl₄⁻) and include data for this compound in Table 3. Careful comparison of the spectra suggests that the complex anions have essentially the same structure in the three compounds. The band close to 280 cm⁻¹, a tellurium-chlorine stretching mode, is strong in the Raman spectrum; it is therefore probably the A₁ mode. The strong infrared band below 230 cm⁻¹ is weak in the Raman spectrum and is probably the E mode, thus leaving the medium to strong Raman band at approximately Δν 250 cm⁻¹ to be assigned as the B₁ mode. These assignments offer reasonable support for the proposed square-based pyramidal structure but interpretation is complicated by the unfortunate overlap of ν(TeCl) with R modes in RTeCl₄⁻.

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